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(54) **Hydrophilic acrylic adhesive.**

(57) A pressure sensitive acrylic adhesive mass is made hydrophilic by blending one or more water/moisture absorbing, water/moisture transmitting substances into the acrylic mass. The resulting adhesive is particularly suited for medical use such as in bandage and wound dressing type products.

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HYDROPHILIC ACRYLIC ADHESIVE

Pressure sensitive adhesive compositions particularly suited for adherence to moist body surface have been disclosed. For example, Chen in United States Patent 3,339,546 discloses such a composition prepared by blending a natural or synthetic viscous gum like substance such as natural rubber, silicone rubber, acrylonitrile rubber, polyisobutylene, which is preferred, etc., and one or more water soluble or swellable hydrocolloids such as sodium carboxymethylcellulose, pectin, gelatin, etc.

Chen in United States Patent 4,192,785 disclose a pressure sensitive adhesive composition particularly useful for attaching an ostomy appliance to the skin. The composition is a blend of certain moisture absorbing hydrocolloid gums such as guar gum or locust bean gum, a pressure sensitive adhesive component such as low molecular weight polyisobutylene or mixtures of low molecular weight polyisobutylene and butyl rubber or medium molecular weight polyisobutylenes, a cohesive strengthening agent such as fibrous materials, cellulosic materials, water insoluble cross-linked dextran, water insoluble cross-linked sodium carboxymethylcellulose, or water-insoluble starch-acrylonitrile graft copolymers, and optionally one or more skin soothing or healing hydrocolloid gums such as pectin or karaya.

Doyle et al. in United States Patent 4,551,490 discloses a pressure sensitive adhesive composition particularly resistant to biological fluids. The composition is a blend of one or more polyisobutylenes or polyisobutylene and butyl rubber, one or more styrene radial or block copolymers, mineral oil, one or more water soluble hydrocolloid gums, and a tackifier.

Chen in United States Patent 3,972,328 and Pawelchak et al. in United States Patent 4,538,603 disclose dressings or bandages having a skin and wound contacting pressure sensitive adhesive layer and a layer of semi-open cell polyurethane foam. The skin contacting adhesive layer contains one or more hydrocolloids dispersed in a rubbery elastomer such as polyisobutylene.

Cilento et al. in European Patent Application 190,814 disclose a wound dressing comprising a closed cell polyurethane foam containing from about 5% to about 50% by weight of the foam of one or more water dispersible, water swellable, and/or water absorbing agents. A pressure sensitive adhesive is laminated as a continuous or discontinuous layer onto one surface of the foam. The adhesive can be an acrylic pressure sensitive adhesive, an acrylic microporous pressure sensitive adhesive, or a polyisobutylene-hydrocolloid containing pressure sensitive adhesive.

Pressure sensitive adhesives have been formulated from acrylics. For example, Ulrich in United States Patent RE24,906 discloses an acrylic based pressure sensitive adhesive from a copolymer of isooctyl acrylate and acrylic acid. Various pressure sensitive acrylic adhesives suitable for use in bandages and wound dressing are disclosed by Hodgson in United States Patents RE31,886 and 31,887, by Gander in United States Patent 3,475,363, by Ono et al. in United States Patents 3,928,262, 3,975,570 and 3,983,297, by Peck in United States Patent 4,379,881, and by Shah in United States Patent 4,510,197.

Hymes et al. in United States Patent 4,307,717 disclose an adhesive bandage containing a medicament. The bandage comprises a flexible backing and a hydrophilic adhesive matrix comprising about 30 to 50% of polyacrylic acid, polyacrylamide and their congeners and a liquid phase consisting of a solution or emulsion of carbohydrate and/or protein, and a medicament such as an anti-inflammatory agent. The solid phase of the matrix can include a gum such as karagen, gum acacia, locust bean gum, and guar gum.

Acrylic adhesive formulations possess several properties that make them particularly useful in medical applications. Acrylic adhesive can be irradiated for sterilization purposes without any significant change in their adhesive properties. Acrylic adhesives are temperature stable and are less prone to cold flow, i.e., the creeping of the adhesive mass away from a backing film, than polyisobutylene based adhesives.

However, despite these advantages, acrylic adhesives suffer from a serious drawback in their lack of adhesion to moist body surfaces and their inability to retain adhesive strength in the presence of moistness. Thus, perspiration which can form under or along the edges of the adhesive layer, moisture from wound exudate, or external moisture from showering or bathing can result in a loss of adhesive strength.

This invention is directed to pressure sensitive hydrophilic acrylic adhesives suitable for use on human skin which retain their adhesive strength in the presence of moisture and/or wound exudate. This result is achieved by incorporating one or more water/moisture absorbing, water/moisture transmitting substances within the acrylic adhesive mass.

Hydrophilic, pressure sensitive, acrylic adhesives suitable for various medical applications are prepared by blending one or more water moisture absorbing, water/moisture transmitting substances into the acrylic adhesive mass. Suitable water moisture absorbing, water/moisture transmitting substances include water soluble and/or water swellable hydrocolloids, one or more "super absorbents", or a mixture of hydrocolloids and "super absorbents".

Suitable hydrocolloids include sodium carboxymethylcellulose, calcium carboxymethylcellulose, pectin, gelatin, guar gum, locust bean gum, collagen, gum karaya, and mixed sodium/calcium salts of alginic acid. These substances result in the acrylic adhesive becoming hydrophilic when present at from about 15% to about 50% by weight of the acrylic adhesive compositions, preferably from about 20% to about 40% by weight of the adhesive composition.

The term "super absorbent" refers to agents capable of absorbing water/moisture in amounts greater than their own weight. Suitable "super absorbents" include substantially water insoluble starch-acrylonitrile graft copolymers such as those described in United States Patent 3,661,815 and those available commercially under the trademark Water Lock from the Grain Processing Corp., water insoluble cross-linked sodium carboxymethylcellulose such as that commercially available under the trademark Aqualon or that described in United States Patent 3,589,364 and commercially available from the Buckeye Cellulose Corp., and substantially water insoluble cross-linked dextran such as that commercially available under the trademark Sephadex. The acrylic adhesive becomes hydrophilic upon the addition of from about 5% to about 20% by weight of such super absorbents, preferably from about 5% to about 15% by weight.

A mixture of super absorbents and hydrocolloids can be employed to render the acrylic adhesive hydrophilic. Suitable mixtures contain from about 5% to about 10% by weight of super absorbents and from about 10% to about 25% by weight of hydrocolloids.

Optionally, other materials may be included within the hydrophilic adhesive composition. For example, small amounts, i.e. less than about 5% by weight, of a pharmaceutically active ingredient such as an antibiotic or antimicrobial agent, an antiseptic agent such as povidone iodine, a fragrance, an antioxidant, etc.

The acrylic mass into which the water absorbing, water transmitting substances are added along with any optional materials can be any acrylic adhesive formulation known to be pressure sensitive and suitable for use on human skin. Suitable acrylics include acrylic esters particularly those with four or more carbon atoms in the alcohol component such as n-butyl acrylate and/or 2-ethylhexyl acrylate. The acrylic adhesive may contain other comonomers such as vinyl acetate, acrylonitrile, styrene, ethyl acrylate, methyl methacrylate, α,β -unsaturated carboxylic acids, esters, or half esters of unsaturated dicarboxylic acids. Terpolymers can also be used for this purpose. A discussion of pressure sensitive acrylic adhesives appears in the Handbook of Adhesives, 2nd Edition, Skeist, pages 543 - 552.

The hydrophilic, pressure sensitive, acrylic adhesive compositions of this invention are suitable for various medical applications. For example, the adhesive can be employed to attach or anchor a medical device to the body such as a female incontinence device as shown by Steer in United States Patent 4,568,339 or the adhesive can be cut into strips to anchor a male incontinence device as shown by Rogers et al. in United States Patent 3,863,638. The adhesive composition can be laminated to a polymeric film or a nonwoven or woven fabric backing and employed as a bandage. Suitable polymeric films include polyethylene, polyurethane and films made from polyether polyamide block copolymers such as films commercially available from resins sold by Atochem under their trademark PEBAX. Suitable nonwoven fabric backings include materials made from polyester fibers, polypropylene fibers, nylon fibers, composite olefin fibers, or cellulosic fibers which are commercially available. Suitable woven fabric backings include cotton, cotton blends, etc. The adhesive composition can also be laminated to a polymeric foam layer and employed as a wound dressing. Suitable polymeric foams include semi-open or open cell polyurethane foams such as those employed by Chen in United States Patent 3,972,328 and Pawelchak et al. in United States Patent 4,538,603 and the flexible closed cell polyurethane foam containing one or more water dispersible, water swellable and/or water absorbing agents employed by Cilento et al in European Patent Application 190,814.

The hydrophilic, pressure sensitive acrylic adhesive compositions of this invention are prepared by blending and mixing the water/moisture absorbing, water/moisture transmitting substances and any optional substances, preferably in finely divided powder form, over a period of time into a slurry or suspension of the acrylic adhesive component in an organic solvent. Any conventional propeller blade type mixer can be employed and the blending is done at room temperature and normally takes from about 15 to 30 minutes and results in an essentially homogeneous adhesive slurry. The resulting adhesive slurry is then cast onto a sheet of release paper or other suitable carrier at the desired thickness. The casting step is done with conventional apparatus such as a knife over roller to a thickness of from about 40 to about 100 mg. of adhesive per square inch depending upon the ultimate use. The adhesive coated release paper is then dried for example by passing through a hot air tunnel to evaporate off the organic solvent. The exposed surface of the adhesive can then be covered by another sheet of release paper, or laminated to a polymeric film, or laminated to a nonwoven or woven fabric backing or to a polymeric foam as described above.

The adhesive compositions of this invention can be sterilized by means of gamma radiation.

The following examples are illustrative of the invention.

Example 1

A wound dressing is prepared as follows.

An acrylic pressure sensitive adhesive slurry (40% solids in toluene/hexane, 30 kg.) commercially available from Avery as AS351 is placed within a propeller blade type mixer. A powdery mixture of sodium carboxymethylcellulose (3.84 kg.), pectin (0.48 kg.) and gelatin (0.48 kg.) is added with mixing over a period of 15 minutes and mixing is continued for an additional 5 minutes to give a homogeneous adhesive slurry.

This adhesive slurry is cast onto a sheet of silicone coated release paper by means of a knife over roller apparatus. The adhesive coated release paper is passed through a drying tunnel having a temperature of about 150° F for about 15 minutes to evaporate off the toluene/hexane solvent to give an adhesive layer of about 75 mg. of dry adhesive per square inch.

The exposed surface of the adhesive is then pressure laminated to an open cell polyurethane foam layer. The resulting wound dressing is cut to shape, packaged, and sterilized.

Example 2

A bandage is prepared by following the procedure of Example 1 except that the adhesive is cast onto the release paper at a thickness of about 40 to about 60 mg. of dry adhesive per square inch. After standing, the exposed adhesive surface is then pressure laminated to a thin film, i.e., about 1 mil. thickness, made from a PEBAX resin (commercially available from Schoeller as Medifilm 827).

Examples 3 - 18

Following the procedures of Examples 1 and 2, additional hydrophilic, pressure sensitive, acrylic adhesive compositions within the scope of this invention can be prepared for use in wound dressing or bandage type products. The ingredients are expressed as the weight percent of the final dried adhesive mass:

| Ingredient | Weight percent of the ingredient within the dried adhesive composition | | | |
|---|--|----|----|----|
| | 3 | 4 | 5 | 6 |
| Acrylics | 70 | 65 | 70 | 90 |
| Sodium carboxymethylcellulose | 10 | 35 | 20 | - |
| Calcium carboxymethylcellulose | - | - | - | - |
| Pectin | 10 | - | - | - |
| Gelatin | 10 | - | - | - |
| Guar gum | - | - | - | - |
| Locust bean gum | - | - | - | - |
| Collagen | - | - | - | - |
| Gum karaya | - | - | - | - |
| Sodium/calcium salt of alginic acid | - | - | - | - |
| Water insoluble starchacrylonitrile graft copolymer(Water Lock A-100) | - | - | 10 | 10 |
| Water insoluble cross-linked sodium carboxymethylcellulose | - | - | - | - |
| Water insoluble cross-linked dextran | - | - | - | - |

| Ingredient | Weight percent based upon total solids of the adhesive formulation | | | |
|---|--|----|----|----|
| | 7 | 8 | 9 | 10 |
| Acrylics | 85 | 65 | 65 | 70 |
| Sodium carboxymethylcellulose | - | 20 | - | - |
| Calcium carboxymethylcellulose | - | - | 20 | - |
| Pectin | - | - | - | 5 |
| Gelatin | - | - | - | 5 |
| Guar gum | - | - | - | 20 |
| Locust bean gum | - | - | 15 | - |
| Collagen | - | - | - | - |
| Gum karaya | - | - | - | - |
| Sodium/calcium salt of alginic acid | - | 15 | - | - |
| Water insoluble starch/acrylonitrile graft copolymer (Water Lock A-100) | - | - | - | - |
| Water insoluble cross-linked sodium carboxymethylcellulose | 15 | - | - | - |
| Water insoluble cross-linked dextran | - | - | - | - |

| Ingredient | Weight percent based upon total solids of the adhesive formulation | | | |
|--|--|----|----|----|
| | 11 | 12 | 13 | 14 |
| Acrylics | 70 | 70 | 70 | 75 |
| Sodium carboxymethylcellulose | 20 | 15 | 20 | 20 |
| Calcium carboxymethylcellulose | - | - | - | - |
| Pectin | - | - | - | - |
| Gelatin | 5 | - | - | - |
| Guar gum | - | - | - | - |
| Locust bean gum | 5 | - | - | - |
| Collagen | - | 10 | - | - |
| Gum karaya | - | - | 10 | - |
| Sodium/calcium salt of alginic acid | - | 5 | - | 5 |
| Water insoluble starch/acrylonitrile graft copolymer(Water Lock A-100) | - | - | - | - |
| Water insoluble cross-linked sodium carboxymethylcellulose | - | - | - | - |
| Water insoluble cross-linked dextran | - | - | - | - |

| Ingredient | Weight percent based upon total solids of the adhesive formulation | | | |
|---|--|----|----|----|
| | 15 | 16 | 17 | 18 |
| Acrylics | 80 | 70 | 55 | 88 |
| Sodium carboxymethylcellulose | 15 | 20 | 25 | - |
| Calcium carboxymethylcellulose | - | - | - | - |
| Pectin | - | - | 10 | - |
| Gelatin | - | - | 10 | - |
| Guar gum | - | - | - | - |
| Locust bean gum | - | - | - | - |
| Collagen | - | - | - | - |
| Gum karaya | - | - | - | - |
| Sodium/calcium salt of alginic acid | - | 10 | - | - |
| Water insoluble starchacrylonitrile graft copolymer(Water Lock A-100) | 5 | - | - | - |
| Water insoluble cross-linked sodium carboxymethylcellulose | - | - | - | - |
| Water insoluble cross-linked dextran | - | - | - | 12 |

Claims

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1. A hydrophilic adhesive composition suitable for use on the human skin comprising a pressure sensitive acrylic adhesive mass containing one or more water/moisture absorbing, water/moisture transmitting substances.

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2. The adhesive composition of Claim 1 wherein said water/moisture absorbing, water/moisture transmitting substances are one or more hydrocolloids selected from the group consisting of sodium carboxymethylcellulose, calcium carboxymethylcellulose, pectin, gelatin, guar gum, locust bean gum, collagen, gum karaya, and mixed sodium/calcium salts of alginic acid, one or more super absorbents selected from the group consisting of substantially water insoluble starch-acrylonitrile graft copolymers, substantially water insoluble cross-linked sodium carboxymethylcellulose, and substantially water insoluble cross-linked dex-

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tran, and mixtures of one or more hydrocolloids and super absorbents.

3. The adhesive composition of Claim 2 wherein said water/moisture absorbing, water/moisture transmitting substances are one or more hydrocolloids present in the hydrophilic acrylic adhesive composition at from about 15% to about 50% by weight of said acrylic adhesive mass.

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4. The adhesive composition of Claim 3 wherein said hydrocolloids are a powdery blend of sodium carboxymethylcellulose, pectin, and gelatin and said blend is present in the hydrophilic acrylic adhesive at from about 20% to about 40% by weight of said acrylic adhesive mass.

5. The adhesive composition of Claim 2 wherein said water/moisture absorbing, water moisture transmitting substances are one or more super absorbents present in the hydrophilic acrylic adhesive composition at from about 5% to about 20% by weight of said acrylic adhesive mass.

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6. The adhesive composition of Claim 5 wherein said super absorbent is a water insoluble starch-acrylonitrile graft copolymer present in the hydrophilic adhesive composition at from about 5% to about 15% by weight of said acrylic adhesive mass.

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7. The adhesive composition of Claim 2 wherein said water/moisture absorbing, water/moisture transmitting substances are a mixture from about 5% to about 10% by weight of said acrylic adhesive mass of one or more super absorbents and from about 10% to about 25% by weight of said acrylic adhesive mass of one or more hydrocolloids.

8. A bandage for use on the human skin comprising a backing layer and a hydrophilic adhesive layer said adhesive layer comprising an adhesive composition according to any preceding claim.

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9. The bandage of Claim 8 wherein said backing layer is a polymeric film, a nonwoven fabric, a woven fabric, or a polymeric foam.

10. A process for preparing the hydrophilic acrylic adhesive composition of any one of Claims 1-7 comprising

a) adding a solution of a pressure sensitive acrylic adhesive in an organic solvent to a propeller type mixer,

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b) blending into said acrylic solution a powder comprising one or more water/moisture absorbing, water/moisture transmitting substances,

c) continuing said blending until a homogeneous slurry is formed,

d) casting said hydrophilic, pressure sensitive, adhesive slurry onto a sheet of release paper, and

e) drying said adhesive slurry in a hot air tunnel to evaporate off said organic solvent.

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| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| Y | EP-A-0 122 344 (E.R.SQUIBB & SONS, INC.) * Page 5, lines 20-35; page 6, lines 1-20; claims * --- | 1-9 | A 61 L 15/06 A 61 L 25/00 |
| Y | US-A-4 505 976 (D.F.DOEHNERT et al.) * Claims * --- | 1-9 | |
| D,A | US-A-4 307 717 (A.C.HYMES et al.) * Claims * --- | | |
| D,A | EP-A-0 035 399 (SMITH AND NEPHEW ASSOCIATED CO., LTD) * Page 1, lines 1-14; claims * --- | | |
| A | EP-A-0 175 562 (JOHNSON & JOHNSON PRODUCTS INC.) * Page 2, lines 11-36; page 4, lines 22-29; page 5, lines 5-14; page 6, lines 31-36; page 7, lines 1-4 * ----- | | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl.4) |
| | | | A 61 L C 09 J |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 07-10-1988 | Examiner ESPINOSA Y CARRETERO M. |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |